OXIDATION BEHAVIOUR OF POLYMER-DERIVED CERAMICS

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1 Introduction

Active works on polymer-derived ceramics (PDC) have been achieved until recently to fulfil high temperature applications in oxidizing environments (*e.g.*, in gas turbines or aeronautic engines). For instance, precursors involving up to five different elements (comprising neither H nor O) have been synthesized to enhance the oxidation and corrosion resistance of the derived ceramics [Muller04]. In most of the studies on PDC, the assessment of the oxidation behaviour is only a part. There are only few systematic studies aiming at comparing the properties of different ceramic systems and discussing, for example, the effect of the free carbon concentration [Brewer99, Chollon00, Modena05] or the addition of a hetero-element [Butchereit00, Muller04, Saha04, Wang05]. This is because the comparison is often rendered difficult by the different characteristics of the initial ceramic (e.g., specific surface, open porosity…) and the variable composition of the resulting oxides.

The present contribution is not a comprehensive review on the behaviour of PDC in all possible oxidizing environments. Neither active oxidation (at high temperature/low pressure) nor corrosion (in presence of H_2O or other combustion gases) will be treated here, because of the lack of reliable data due to the complex control of the gas phase (temperature, partial pressures, gas velocity). This work will rather be based on a materials science approach, relating a wide range of PDC features to regular (i.e., usually passive) oxidation behaviour.

First of all, the various experimental procedures used to evaluate the oxidation behaviour of PDC will be reviewed. The choice of a certain method among others indeed depends on the conditions in service, but is also dictated by the geometry of the specimens (particles, porous monoliths, fibres…). In a second step, the oxidation behaviour in pure oxygen or dry air of PDC

belonging to various systems will be described, with a growing degree of complexity, *i.e.*, from binary to quaternary or even more complex systems.

2 Materials geometry and experimental procedures

Studies of reference on the oxidation of Si-based ceramics often refer to ideally pure, dense, flat and smooth materials (mirror-polished single crystals or polycrystalline CVD coatings) [Du89, Ramberg96]. Oxidation kinetics are then assessed using specific tools for flat and thin layers of well defined oxide (*e.g.*, ellipsometry, SIMS, RBS). These approaches are neither compatible with the application requirements nor the processing constraints of PDC.

Due to the shrinkage and the gas evolution during pyrolysis, dense PDC monoliths or crack-free coatings are hard to obtain. The pyrolysis of the green or cured free standing polymer results in relatively coarse and foamy residues, depending on the precursor viscosity and ceramic yield. Only post-grinding can eliminate porosity and adjust the specific surface to a certain extent. Crack-free monolith can be obtained by hybrid processing, but the open porosity at low scale is still present [Raj01]. Alternatively crack-free monolithic Si-C-O can be processed from gel-derived precursors [Soraru96, Walter04].

If the extent of oxidation is assessed by direct thickness measurements of the oxide layer, the geometry of the specimen is only of minor concern. However, it is necessary to avoid a rate limitation by gas phase diffusion through the open porosity of the solid. Otherwise, the thickness may not be homogeneous and kinetics may be underestimated. This applies for porous materials but also for high surface/volume ratios (*e.g.*, powders) and especially at high temperature, at the beginning of oxidation, when the oxidation rate is the highest. Furthermore, the thickness of the oxide layer may also be altered by the viscous flow at high temperature (particularly for B-rich ceramics, see§6).

Another obvious way to evaluate the oxidation extent is the weight change. This is advantageous especially when achieved in situ by TGA [Chollon00]. Within a passive regime, the weight change resulting from oxidation can generally be predicted by assuming the formation of non-volatile oxides of well-defined composition and the evolution of CO and N_2. The case of boron-containing ceramics is more delicate as the volatilization of B_2O_3 is significantly activated in dry air beyond 1000°C (see§6).

Three parameters characterizing the oxidation extent: the relative weight change, the thickness of the oxide layer and the consumed ceramic, can be related one to each other. These relations are often linear and involve material features such as a reacting surface constant (*e.g.*, initial specific surface, average fibre or particle diameter), the initial weight concentrations of the oxide formers and the densities of the initial ceramic and the oxide [Chollon00, Butchereit01b]. Two other constants are sometimes considered to compare the behaviour of ceramics having different compositions. Δ is the volume of oxide formed per volume of ceramic oxidized [Chollon00] and characterizes the volume expansion during oxidation, favourable to a passive regime. α, the number of mole of O_2 needed to form one mole of oxide, is used to compare the parabolic oxidation rates of various ceramics. αK_p is indeed preferred to K_p (the oxide thickness parabolic constant), as it rather reflects the inward O_2 flux (usually limiting in case of a passive regime) [Luthra91].

Ideally, the material tested should be homogeneous in terms of chemical composition and structure. Its initial reacting surface should be known and the geometry change during oxidation of both the oxide layer and ceramic easily predictable. TGA is appreciable but requires specimens with high specific surfaces. Fibres are materials of choice, as they are dense, homogeneous and have adequate specific surfaces ($\geq 0.1 m^2 g^{-1}$). But the main advantage of fibres compared to powders is their higher gas permeability and few contact points limiting coalescence of adjacent oxide layers.

3 The Si-C system

As most of PDC, those belonging to the Si-C system often contain free turbostratic carbon. This phase may also be partially hydrogenated when pyrolysed at insufficiently high temperature (T_p) [Shimoo03]. The SiC phase is predominantly β and nanometric ($\leq$10nm) or submicrometric ($\leq$60nm) in scale. The SiC grain size generally decreases with the amount of free carbon and increases with T_p [Ichikawa06]. The SiC+C system is one of the most stable from a thermodynamical point of view.

This intrinsic thermostability gives rise to a regular oxidation behaviour in pure O_2 or dry air of SiC+C PDC. A parabolic growth regime of a pure silica layer is observed from 800 to 1400°C with constant activation energy of about $100 kJmol^{-1}$. This behaviour concludes to a mechanism limited by the inward permeation of O_2 through the growing SiO_2 layer, CO diffusing

readily outwards [Chollon00, Naslain04]. This mechanism is fundamentally the same as that reported for silicon or pure SiC [Ramberg96]. The activation energies are close and the parabolic constants K_p depend on the O_2 partial pressure [Naslain04] and the carbon content (through α). Amorphous SiO_2 starts to crystallizes into cristobalite at about 1200-1300°C. After few hours at 1400°C, the layer is substantially crystalline, but this phenomenon does not result in a significant increase of the oxidation rate [Chollon00, Naslain04].

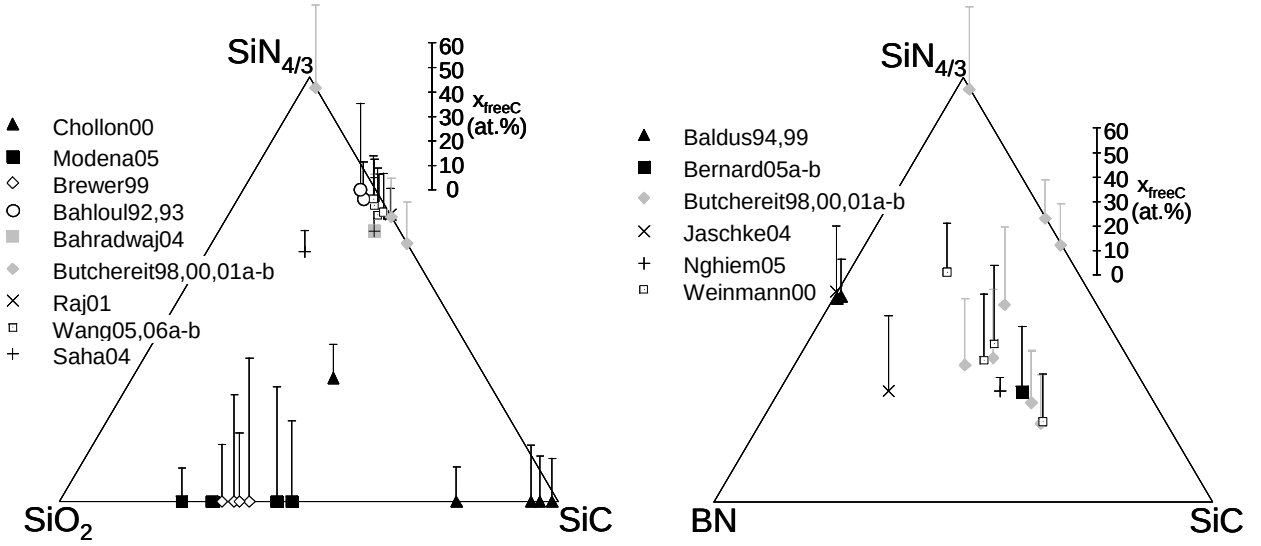
This behaviour is not obeyed in case of incomplete ceramization. The free carbon phase releases hydrogen and the H_2O outward diffusion through SiO_2 accelerates dramatically the initial oxidation [Chollon00, Shimoo03]. Beyond 1400°C, a catastrophic transition in the kinetics is usually observed. A successive oxide decohesion is indeed observed, probably due to the CO pressure build up at the interface and the high viscosity of the highly crystalline SiO_2 layer [Chollon00].

4 Si-C-O sytem

PDC from the Si-C-O system are usually polycrystalline SiC-based or silicon oxycarbides. The former consists mainly of β-SiC nanocrystals (~2-3nm), whereas the latter is essentially amorphous. Both contain an amorphous $SiC_xO_{2(1-x)}$ phase and free aromatic carbon partially hydrogenated (depending on T_p). The silicon oxycarbide phase is usually more abundant and the free carbon amount more variable in glasses than in crystalline ceramics (Fig. 1a). The Si-C-O system is thermodynamically unstable compared with SiC+C and decomposes beyond ~1200°C into SiC, SiO and CO. At low temperatures, the material undergoes a structural evolution (without chemical change). A redistribution of the mixed tetrahedral environment (SiC_XO_{4-X}) into SiC_4/SiO_4 sites and a dehydrogenation/condensation of the free carbon phase are noticed when T_p increases [Hurwitz99]. At larger range, a slight SiC crystal growth occurs in crystalline Si-O-C, whereas the glass remains amorphous. Such a wide range of chemical composition and structure and their intrinsic thermally activated changes during oxidation cause singular behaviours.

As for Si-C PDC, if Si-C-O glasses are pyrolysed at a very low temperature ($T_p \leq 800$°C) and still contain $Si-CH_3$ and Si-OH groups, their oxidation behaviour is catastrophic beyond 600°C [Zhang92]. CH_3 groups are oxidized into CO before the complete formation of the aromatic carbon network and ruins the material. For higher T_p values (T_p=1000-1200°C), the

growth of a protective SiO_2 layer on a Si-C-(O) fibre is observed but the presence of residual hydrogen and the H_2O diffusion accelerate the initial oxidation kinetics at 1500°C [Shimoo03].



(a) (b)

Figure 1 : Compositions of the various PDC submitted to oxidation tests. (a) Si-(X)-C-(N)-(O) (X concentration neglected) and (b) Si-(X)-B-C-N-(O) system (X and O concentration neglected).

Hurwitz and Meador investigated the influence of T_p on the structure of the as-pyrolysed and oxidized Blackglas^{TM} [Hurwitz99]. The surface of the powder specimens was controlled so that the quantification of the various SiC_XO_{4-X} sites by ^{29}Si NMR could provide the oxidation extent. The oxidation rate is clearly reduced when T_p increases. This behaviour is explained by the redistribution of the more oxidation-prone SiC_2O_2 and $SiCO_3$ sites into SiO_4 and SiC_4, as T_p increases. In this study, the role of the free carbon phase and particularly its dehydrogenation (likely significant within T_p=900-1100°C) is not taken into account. Furthermore, the morphology and the thickness of the SiO_2 layer were not examined to confirm the passive oxidation regime and correlate with the RMN data.

Silicon oxycarbide glasses were obtained from the pyrolysis (T_p=1200°C) of various polymers and sol-gels yielding free carbon atomic concentration (x_{freeC}) ranging from ~0 to 59at% (46wt%) [Brewer99, Modena05]. The oxidation behaviour (from 600 to 1350°C in air) was evaluated by weight change and elemental analyses of fine powders (≤100μm), morphology examinations and thickness measurements of the SiO_2 layer and from n-RBS depth profiling of

ceramic monoliths [Vomiero03]. The oxidation rate of the ceramics having the highest free carbon levels is significantly higher than that of the other specimens at all temperatures, but most particularly at the lowest temperatures (600-800°C). The percolation of the oxidizing free carbon phase and the too low reactivity of the silicon oxycarbide allow the reaction to proceed throughout the entire material [Brewer99]. This phenomenon is lessened at higher temperatures (1000-1200°C), the silicon oxycarbide, readily oxidized, forming a more protective silica layer, limiting the O_2-diffusion into the bulk. The n-RBS profiles reveal that at 1150°C in air, the concentration profile at the SiO_2/ceramic interface is gradual at the early oxidation stage and becomes steep after a long time [Vomiero03]. This suggests a transition in the oxidation mechanism from a limitation by a mixed diffusion/reaction mechanism at the early stages of oxidation to a pure diffusion mechanism for longer times. The former mechanism is likely associated with the presence of free carbon, the transition being faster when x_{freeC} is higher. A parabolic kinetic regime is observed at 1350°C in air for various free carbon contents (from x_{freeC}~0 to 47at%) [Modena05]. K_p values are considerably higher than those obtained for SiC or Si-C and Si-C-(O) fibres (Fig. 2), possibly due to an insufficient pyrolysis temperature and/or to the inherent instability of the oxycarbide phase. A slight increase of αK_p is noticed when x_{freeC} increases, which has been related to the carbon activity (actually the atomic concentration) of the substrate. This argument, based on a local thermodynamic equilibrium, remains questionable as the substrate itself ($SiC_xO_{2(1-x)}$+free C) is not at equilibrium.

Si-C-(O) fibres with various oxygen (x_O=1-16at%) and free carbon(x_{freeC}=14-23at%) concentrations were also submitted to oxidation tests in pure oxygen. All these fibres demonstrate a parabolic regime similar to bulk SiC [Chollon00]. However, a catastrophic growth of the oxidation rate is observed beyond 1200°C for the oxygen-rich fibres. This behaviour was attributed to the thermal decomposition of the $SiC_xO_{2(1-x)}$+free C system, SiO and CO gases blowing the SiO_2 layer out of the substrate.

5 Si-(X)-C-N-(O) systems

PDC belonging to Si-C-N-(O) systems are usually processed from commercial or experimental [Bahloul92,93] poly(carbo)silazane precursors. The precursors are sometimes modified with the introduction of a heteroelement X (X=Zr, Al…) [Saha04, Wang05,06a-b] and oxygen can also be introduced simultaneously [Saha04] or during curing to get infusible fibres

[Chollon00]. The ceramic obtained after pyrolysis in inert atmosphere generally consists of a metastable amorphous silicon oxycarbonitride phase $SiC_xN_{4y/3}O_{2(1-x-y)}$) with a mixed $SiC_XN_YO_{4-X-Y}$ tetrahedral environment and free aromatic carbon (Fig.1a) [Chollon00]. A pyrolysis in a NH_3 atmosphere gives rise to a nearly carbon-free Si-N-O ceramic [Bahloul92]. Si-C-N-O materials are slightly more stable than those from the Si-C-O system, especially under a N_2 atmosphere. Beyond 1300°C, they decompose into SiO, CO, N_2 and crystalline SiC. Even in absence of oxygen, the carbon excess reacts with the silicon nitride phase to form SiC and N_2 beyond 1480°C [Monthioux96, Nickel99, Seifert02].

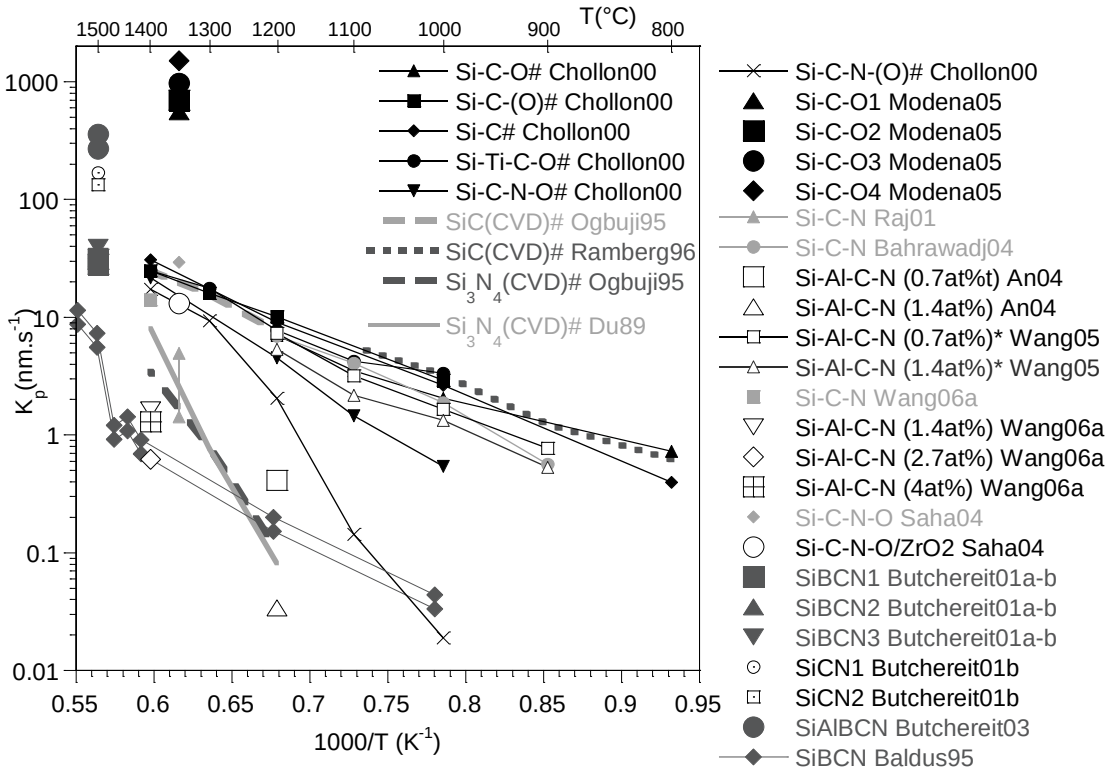


Figure 2 : Effect of temperature on the parabolic oxidation rate K_p, the various PDC (see Fig. 1). Experiments performed in air (except #: in pure O_2), P=100kPa. *initial rate (non stationary).

Bahloul et al. studied the oxidation behaviour of Si-C-N ceramic powders with different carbon contents and at different T_p, by mean of TGA and mass spectrometry analysis [Bahloul92,93]. They showed that the mechanism of oxidation depends on the initial microstructure, itself influenced by the pyrolysis conditions. The selective oxidation of free

carbon facilitates the oxygen diffusion and the oxidation of the silicon carbonitride. This phenomenon is enhanced by a larger amount of free carbon but also by increasing T_p. At T_p=1400°C, the segregation of the free carbon/Si_3N_4 phases and the ceramic microcracking improve the accessibility to oxygen. Conversely at T_p=1200°C, the carbon phase is dispersed in the silicon carbonitride and is therefore less vulnerable to oxidation. Furthermore, the presence of residual hydrogen may also activate the formation of silica protecting free carbon from further oxidation. A similar trend is noticed for substantially crystalline Si-C-N ceramics obtained at much high temperatures (T_p=1540°C/N_2), the coarser microstructure and the larger pore channels indeed resulting in enhanced oxidation rates [Ziegler99].

For the reasons stated in §2, the TGA of porous monoliths or fine powders gives rise to complex weight gains versus time. These functions were however modelled using exponential and Z-L-T equations, respectively [Raj01]. A parabolic constant K_p was deduced from the latter for the oxidation of Si-C-N ceramic at T=1350°C in ambient air, which approaches that for pure Si_3N_4 (Fig. 2). Other authors studied the oxidation of dense Si-C-N-O monoliths and fine fibres. These studies showed the formation of a dense and continuous oxide layer (without bubbles or cracks), with a sharp oxide/ceramic interface and revealed parabolic e(t) and $\Delta m/m_0(t)$ laws within the whole experimental domain (T=800-1400°C, P=100kPa of O_2 or air) [Chollon 00, Bharadwaj04]. The parabolic constants and the activation energies (E_a) were found to fall in with the values obtained for pure SiC and Si_3N_4 (Fig. 2). Whereas the oxygen and free carbon concentrations have only a little influence, the increase of the nitrogen ratio y (and the decrease of the carbon ratio x) in the silicon oxycarbonitride phase induces a significant decrease of K_p at low temperatures and increase of E_a (up to about 300kJmol^{-1}) [Chollon00]. This specific property of nitrogen-containing PDC was related to the well distinct oxidation behaviour of SiC and Si_3N_4 and particularly the significantly higher E_a value for the latter [Du89, Ogbuji95, Ramberg96]. The oxidation behaviour of Si-C-N-(O) ceramics was attributed to a complex O_2-permeation/reaction limited kinetic regime involving the formation of an intermediate silicon oxynitride layer, as already asserted for Si_3N_4 [Sheldon96].

Recently, Wang et al. reported on the oxidation resistance of Si-Al-C-N ceramics obtained by the modification of a commercial precursor with an aluminium alkoxide [Wang05-06a-b]. Variable amounts of aluminium were introduced in the ceramic (up to 4at% after pyrolysis). The oxidation kinetics were measured in dry air at 900-1400°C and compared to those of the Al free

Si-C-N ceramic. Whereas the latter shows a typical parabolic behaviour, the oxidation rate of the Si-Al-C-N materials is non-parabolic for T≥1000°C and decreases more rapidly with time, at a negligible level [Wang05]. At T=1400°C, a stationary parabolic rate is observed for t>20h, with parabolic constants about ten times lower than those of the Si-C-N specimen (Fig. 2) [Wang06a]. This anomalous behaviour was attributed to the Al atoms, (partly) sitting in the six-membered SiO_4 rings, impeding the O_2 permeation and therefore reducing the oxidation rate. Recent SIMS analyses of the ^{18}O tracer diffusion at 1050°C confirmed that the oxidation of Si-Al-C-N ceramics, as for Si-C-N, is controlled by interstitial diffusion and that the diffusion rate is much lower in the Al-containing silica than in pure SiO_2 formed on Si-C-N [Wang06b].

Alternatively, Saha et al. compared the oxidation of Si-Zr-C-N-O fibres and Si-C-N ceramic, in air at 1350°C [Saha04]. A parabolic regime was observed for both materials and αK_p for Si-Zr-C-N-O was about half the value for Si-C-N. In contrast to Wang et al. for Si-Al-C-N, these authors explain the lower oxidation rate by the lower carbon activity (in fact the lower carbon content) in the starting ceramic, as already proposed for Si-C-O glasses of various free carbon concentrations (see §4) [Modena05].

6 The Si-(X)-B-C-N system

Extensive works on Si-B-(C)-N ceramic precursors were carried out mainly by German and few other research groups [Baldus95,97,99, Jansen97,02, Weinman00, Bernard05a-b]. These precursors were successively spun into fibres and coatings, or hot pressed, and subsequently pyrolyzed. The pyrolysis is achieved under a N_2 or NH_3 atmosphere, yielding Si-B-C-N or Si-B-N ceramics, respectively [Baldus95]. Most of the compositions are located in the Si_3N_4+SiC+C+BN tetrahedral phase field, few of them ("$SiBN_3C$"-type) lying near the Si_3N_4+C+BN section (Fig. 1b) [Seifert02]. The most remarkable feature of Si-B-C-N PDC, compared to Si-C-N, is that they remain chemically stable and nearly amorphous in a N_2 atmosphere up to very high temperatures (T_p~1900°C). For compositions near the Si_3N_4+C+BN section, ^{29}Si, ^{11}B and ^{15}N NMR analyses evidenced a fourfold SiN_4 tetrahedral and a BN_3 trigonal planar coordination of Si and B atoms, respectively [Jansen97,02]. Carbon atoms are rather sp^2 hybridized and incorporated apart from the previous Si-B-N network, in free aromatic carbon, as for the Si-C-N system (as suggested by Raman spectroscopy [Butchereit98]) and/or in a

turbostratic B-C-N phase (C-N bonds being evidenced by X-ray photoelectron spectroscopy [Baldus97]).

The first reports on the oxidation of on Si-B-C-N alleged an outstanding oxidation resistance. A parabolic growth rate was observed up to 1600°C in air, with K_p constants lower than those for Si_3N_4 and SiC [Baldus95]. αK_p is shown in Figure 2 for B-rich PDC, considering either only SiO_2 or both SiO_2 and B_2O_3 in the oxide. This high oxidation resistance was attributed to the formation of a dual surface layer resulting from oxidation (i.e., a SiO_2 outer layer containing B and C traces and a B-N-O inner layer with traces of Si and O), assumed to be more protective from O_2-inner diffusion than a pure SiO_2 layer. Several authors failed to evidence such a double layer [Butchereit00,01]. It was however confirmed and further detailed by few others, who examined "$SiBN_3C$"-type fibres oxidized at 1500°C by TEM [Braue01, Cinibulk01], as well as predicted by thermodynamic calculations [Nickel99].

Contrasting with Si-C-N and Si-C PDC, the TGA shows that Si-B-C-N ceramics undergo much lower weight gains for T<1200-1300°C and sometimes a slight weight loss increasing at higher temperatures [Baldus97, Butchereit98, Bernard05a, Jaschke04]. This is explained by the lower Si content of the initial ceramic, reducing the SiO_2 yield with respect CO and N_2, but also by the superficial volatilization of B_2O_3 from the borosilicate layer, activated at high temperature.

The oxidation behaviour of various Si-B-C-N PDC has been extensively studied by Butchereit et al. Insufficient pyrolysis temperature (T_p=1000-1100°C) leads to a catastrophic oxidation behaviour beyond 1250°C [Butchereit98]. Residual hydrogen is released, producing H_2O, altering the properties of the borosilicate and accelerating the volatilisation of B_2O_3. Even after stabilization (T_p=1320°C), the oxidation behaviour remains complex due to multiple interacting effects. Bubble formation is observed preferentially on dense monolithic ceramics (rather than smaller foamy fragments), at the sharp edges and at high temperature [Butchereit98,00,01a-b]. This heterogeneous behaviour is likely related to the particularly low viscosity of the oxide (due to the incorporation of B_2O_3 in the silica). The oxide flows away from the edges and accumulates in pores, cracks and contact points. The oxide-depleted edges are therefore more exposed to O_2 and a high reaction rate at the interface may result in a pressure build up of product gases. Furthermore, the superficial volatilization of B_2O_3 induces a local increase of viscosity and can give rise to devitrification into cristobalite at high temperature. The discrepancy between monoliths and foamy fragments with high specific surface might be due to

the stagnation of product gases (N_2, CO or volatilized B_2O_3) over the surface, limiting the O_2 inward diffusion or B_2O_3 volatilization in the latter case.

The oxidation rates of three different Si-B-C-N ceramics were assessed by oxide thickness measurements after isothermal tests in air at 1500°C and compared to those of two Si-C-N ceramics [Butchereit01a-b]. Parabolic growth rates were observed only for two Si-B-C-N specimens. Compared to SiC and Si_3N_4, the parabolic constants K_p were found higher for Si-C-N and lower for Si-B-C-N (Fig. 2). However, the calculated recession rate of Si-B-C-N equals that of Si_3N_4. These data were correlated with weight change measurements. All the Si-B-C-N specimens showed negligible weight change, confirming that the predictable gain due to the formation of the borosilicate was at least partially counteracted by the B_2O_3 volatilization [Nickel99, Jacobson01].

Recently, a Si-B-C-N precursor was modified to introduce various amounts of Al (3-7at.%) [Butchereit03, Muller04]. TGA oxidation tests of ceramic particles in O_2 revealed a moderate weight gain increasing from 1100 to 1500°C. At 1500°C, a similar test on a monolith showed a weight loss, suggesting again a rate limitation by gas diffusion through the porosity. Contrasting with Si-B-C-N ceramics, the oxide is well adherent and bubble free. A nearly parabolic law is observed at 1500°C, but with a K_p value higher than those for SiC and Si_3N_4 (Fig. 2).

7 Conclusion

For all chemical systems, regular (parabolic) oxidation rates are observed provided PDC are inherently stable, i.e. (i) T_p is sufficiently high to avoid the H_2/H_2O release from the pre-ceramic and (ii) the system is thermochemically stable to prevent decomposition, e.g., of oxycarb(onitr)ides+free C into SiO, CO, (N_2). For instance, oxygen-rich Si-C-O ceramics should not be used over about 1200°C [Chollon00, Modena05]. Also, whereas a passive oxidation regime is observed for Si-C-N up to 1400°C, the severe increase of the oxidation rate at 1500°C [Butchereit01b] is likely due to the reaction between silicon nitride and free carbon. The thermal stability of the Si-B-C-N system is significantly higher [Seifert02]. The bubble formation in the oxide observed at 1500°C [Butchereit98, 00, 01a-b] is more likely related to the overpressure of oxidation products at the interface, than that of decomposition gases. A harmful oxidation regime of the ceramic may also be observed if the free carbon phase is too abundant, segregated (for high

T_p), if the silicon oxycarb(onitr)ide reactivity is too low and the oxide not protective (i.e., at low temperature) [Brewer99, Bahloul92,93].

Within the intrinsic thermal stability domain, the parabolic rate K_p depends essentially on the nature of the oxide. All Si-C-(O) PDC display similar oxidation behaviours (E_a~100kJmol^{-1}). Conversely, the increase of the nitrogen concentration in Si-C-N-(O) ceramics gives rise to an increase of E_a (up to~300kJmol^{-1}) and decrease of K_p (or αK_p) at low temperatures, close to the values for Si_3N_4 [Chollon00, Raj01].

The influence of further heteroelements is variable. Only a slight decrease of K_p was noticed at 1350°C after the addition of ZrO_2 in Si-C-N PDC, assigned to a free carbon concentration effect [Saha04]. Conversely for T≥1000°C, the addition of aluminium in Si-C-N PDC leads to a remarkable decrease of the oxidation rate after a transient stage, which was explained by the modification of the SiO_2 network [An04, Wang05,06a]. However, this peculiar high temperature transitory regime and particularly the high initial oxidation rates, close to those for SiC, still have to be fully elucidated.

The role of boron in the oxidation rate of Si-B-C-N ceramics is particularly complex. The exceptionally low oxidation rates initially reported [Baldus95] might have been somehow underestimated for several reasons, e.g., the low oxide/ceramic volume ratio, the borosilicate viscous flow and/or the B_2O_3 volatilization …) [Nickel99, Jacobson01]. Furthermore, the dual B-N-O/SiO_2 layer, though observed by few authors, was not clearly demonstrated to slow down the O_2-inward diffusion. More recent studies reported K_p (or αK_p) values close to those for SiC and Si_3N_4 at 1500°C [Butchereit01a-b], concluding to a common rate limiting regime, though significantly complicated by the combination of the above-mentioned effects (e.g., bubble formation). A further addition of aluminium in the Si-B-C-N ceramic was detrimental to the oxidation resistance at 1500°C [Butchereit03], indicating no sign of B_2O_3 stabilization. Clearly there is a lack of data on the oxidation behaviour of Si-(X)-B-C-N PDC at low and intermediate temperatures (800-1000°C). This is regrettable since the use of these borosilicate formers may be valuable in crack healing within this particular temperature range.

Several other features besides plain oxidation should be carefully examined to appraise a new PDC composition for a high temperature structural application. In real use, this component is likely to be associated with different materials, submitted to other corrosive species than O_2 and often to stress. The reactivity between the oxide products and the other nearby materials, the

corrosion under a H_2O environment and the delayed fracture in these aggressive media appears therefore particularly worth considering [Nickel99, Jacobson01].

References

An L, Wang Y, Bharadwaj L, Zhang L, Fan Y, Jiang D, et al. 2004 Silicoaluminum carbonitride with anomalously high resistance to oxidation and hot corrosion. Advanced Engineering Materials. 6(5):337,340+275.

Bahloul D, Pereira M, Goursat P. 1992 Silicon carbonitride derived from an organometallic precursor. influence of the microstructure on the oxidation behaviour. Ceramics International.18(1):1-9.

Bahloul D, Goursat P, Lavedrine A. 1993 Influence of microstructural changes on the oxidation resistance of silicon carbonitrides derived from a polyvinylsilazane. Journal of the European Ceramic Society. 11(1):63-8.

Baldus HP, Jansen M, Wagner O. 1994 New materials in the system Si-(C,C)-B and their characterization. Key Engineering Materials. 89-91:75-80.

Baldus HP, Passing G, Sporn D, Thierauf A. 1995 Si-B-(N,C) a new ceramic material for high performance applications. Ceramic Transactions, 58(High-Temperature Ceramic-Matrix Composites II), 75-84. Publisher: American Ceramic Society.

Baldus H-, Jansen M. 1997 Novel high-performance ceramics - amorphous inorganic networks from molecular precursors. Angewandte Chemie (International Edition in English). 36(4):329-43.

Baldus P, Jansen M, Sporn D. 1999 Ceramic fibers for matrix composites in high-temperature engine applications. Science. 285(5428):699-703.

Bernard S, Weinmann M, Gerstel P, Miele P, Aldinger F. 2005a Boron-modified polysilazane as a novel single-source precursor for SiBCN ceramic fibers: Synthesis, melt-spinning, curing and ceramic conversion. Journal of Materials Chemistry. 15(2):289-99.

Bernard S, Cornu D, Miele P, Weinmann M, Aldinger F. 2005b Polyborosilazane-derived ceramic fibers in the Si-B-C-N quaternary system for high-temperature applications. Ceramic Engineering and Science Proceedings. 26(2):35-42.

Bharadwaj L, Wang Y, Xu W, Dhamne A, An L. 2003 Synthesis and oxidation behavior of polymer-derived Si-Al-C-N and SiCN amorphous ceramics. Advanced Ceramic Engineering and Science Proceedings. 24(4):303-308.

Bharadwaj L, Fan Y, Zhang L, Jiang D, An L. 2004 Oxidation behavior of a fully dense polymer-derived amorphous silicon carbonitride ceramic. Journal of the American Ceramic Society. 87(3):483-6.

Braue W, Paul G, Baldus HP. 2001 Microstructural response of $SiBN_3C$-fibers upon annealing in oxidizing and reducing atmospheres. Editor(s): Krenkel W, Naslain R, Schneider H. High Temperature Ceramic Matrix Composites, [4th International Conference on High Temperature Ceramic Matrix Composites], 96-98. Publisher: Wiley-VCH Verlag GmbH, Weinheim, Germany

Brewer CM, Bujalski DR, Parent VE, Su K, Zank GA. 1999 Insights into the oxidation chemistry of SiOC ceramics derived from silsesquioxanes. Journal of Sol-Gel Science and Technology. 14(1):49-68.

Butchereit E, Nickel KG. 1998 Oxidation behaviour of precursor derived Si-(B)-C-N-ceramics. Journal of Materials Processing and Manufacturing Science. 7(1):15-21.

Butchereit E, Nickel KG. 2000 Oxidation behaviour of precursor derived ceramics in the system si-(B)-C-N. Key Engineering Materials. 175:69-78.

Butchereit E, Nickel KG, Müller A. 2001a Precursor-derived si-B-C-N ceramics: Oxidation kinetics. Journal of the American Ceramic Society. 84(10):2184-8.

Butchereit E, Nickel KG. 2001b Comparison of the oxidation kinetics of boron free and boron containing precursor derived ceramics. Proceedings - Electrochemical Society, 12(High Temperature Corrosion and Materials Chemistry III), 112-123. Publisher: Electrochemical Society.

Butchereit E, Nickel KG. Beneficial effect of aluminum on the oxidation behavior of precursor-derived ceramics. 2003 Proceedings - Electrochemical Society, 16(High Temperature Corrosion and Materials Chemistry IV), 325-338. Publisher: Electrochemical Society.

Chollon G. 2000 Oxidation behaviour of ceramic fibres from the Si-C-N-O system and related sub-systems. Journal of the European Ceramic Society. 20(12):1959-74.

Cinibulk MK, Parthasarathy TA. 2001 Characterization of oxidized polymer-derived SiBCN fibers. Journal of the American Ceramic Society. 84(10):2197-202.

Du H, Tressler RE, Spear KE, Pantano CG. 1989 Oxidation studies of crystalline CVD silicon nitride. Journal of the Electrochemical Society. 136(5):1527-36.

Hurwitz FI, Meador MAB. 1999 Tailoring silicon oxycarbide glasses for oxidative stability. Journal of Sol-Gel Science and Technology. 14(1):75-86.

Ichikawa H. 2006 Development of high performance SiC fibers derived from polycarbosilane using electron beam irradiation curing-a review. Journal of the Ceramic Society of Japan. 114(1330):455-60.

Jacobson NS, Opila EJ, Lee KN. 2001 Oxidation and corrosion of ceramics and ceramic matrix composites. Current Opinion in Solid State and Materials Science. 5(4):301-9.

Jansen M. 1997 Highly stable ceramics through single source precursors. Solid State Ionics. 101-103(PART 1):1-7.

Jansen M, Jäschke B, Jäschke T 2002 Amorphous multinary ceramics in the Si-B-C-N system. High Performance Non-Oxide Ceramics I, Editor: Jansen M. Structure & Bonding Vol 101, 137-191. Publisher: Springer-Verlag, Berlin, Germany.

Jäschke T, Jansen M. 2004 Synthesis and characterization of new amorphous Si/B/N/C ceramics with increased carbon content through single-source precursors. Comptes Rendus Chimie. 7(5):471-82.

Modena S, Sorarù GD, Blum Y, Raj R. 2005 Passive oxidation of an effluent system: The case of polymer-derived SiCO. Journal of the American Ceramic Society. 88(2):339-45.

Monthioux M, Delverdier O. 1996 Thermal behavior of (organosilicon) polymer-derived ceramics. V: Main facts and trends. Journal of the European Ceramic Society. 16:721-37.

Müller A, Gerstel P, Butchereit E, Nickel KG, Aldinger F. 2004 Si/B/C/N/Al precursor-derived ceramics: Synthesis, high temperature behaviour and oxidation resistance. Journal of the European Ceramic Society. 24(12):3409-17.

Naslain R, Guette A, Rebillat F, Le Gallet S, Lamouroux F, Filipuzzi L, Louchet C. 2004 Oxidation mechanisms of SiC-matrix composites and their constituents. Journal of Materials Science, 39 7303-16.

Nghiem Q, Kim D. 2005 Highly-resistant SiCBN films prepared by a simple spin-coating process with poly(borosilazane). Journal of Materials Chemistry. 15(22):2188-92.

Nickel KG. 1999 Corrosion: no problem for precursor-derived covalent ceramics? Precursor-Derived Ceramics: Synthesis, Structures and High Temperature Mechanical Properties, Editor: Bill J, Wakai F, Aldinger F. 188-196. Publisher: Wiley-VCH, Weinheim, Germany.

Obgbuji LUJT, Opila EJ 1995 A comparison of the oxidation kinetics of SiC and Si_3N_4. Journal of Electrochemical Society. 142(3):925-30.

Raj R, An L, Shah S, Riedel R, Fasel C, Kleebe H. 2001 Oxidation kinetics of an amorphous silicon carbonitride ceramic. Journal of the American Ceramic Society. 84(8):1803-10.

Ramberg CE, Cruciani G, Spear KE, Tressler RE, Ramberg Jr. CF. 1996 Passive-oxidation kinetics of high-purity silicon carbide from 800° to 1100°C. Journal of the American Ceramic Society. 79(11):2897-911.

Saha A, Shah SR, Raj R. 2004 Oxidation behavior of SiCN-ZrO2 fiber prepared from alkoxide-modified silazane. Journal of the American Ceramic Society. 87(8):1556-8.

Seifert HJ, Aldinger F. 2002 Phase equilibria in the Si-B-C-N system. High Performance Non-Oxide Ceramics I, Editor: Jansen M. Structure & Bonding Vol 101, 1-58. Publisher: Springer-Verlag, Berlin, Germany.

Sheldon BW. 1996 Silicon nitride oxidation based on oxynitride interlayers with graded stoichiometry. Journal of the American Ceramic Society. 79(11):2993-6.

Sorarù GD, Dallapiccola E, D'Andrea G, 1996 Mechanical Characterization of Sol-Gel-derived Silicon Oxycarbide Glasses. Journal of the American Ceramic Society, 79 (8): 2074-80.

Vomiero A, Modena S, Soraru GD, Raj R, Blum Y, Della Mea G. 2003 Investigation on the oxidation process of SiCO glasses by the means of non-rutherford backscattering spectrometry. Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms. 211(3):401-7.

Walter S, Soraru GD, Brequel H, Enzo S, 2004 Microstructural and Mechanical Characterization of Sol Gel-Derived SiOC Glasses. Journal of the European Ceramic Society, 22(13): 2389-2400.

Wang Y, An L, Fan Y, Zhang L, Burton S, Gan Z. 2005 Oxidation of polymer-derived SiAlCN ceramics. Journal of the American Ceramic Society. 88(11):3075-80.

Wang Y, Fan Y, Zhang L, Zhang W, An L. 2006a Polymer-derived SiAlCN ceramics resist oxidation at 1400 °C. Scripta Materialia. 55(4):295-7.

Wang Y, Sohn Y, Fan Y, Zhang L, An L. 2006b Oxygen diffusion through al-doped amorphous SiO2. Journal of Phase Equilibria and Diffusion. 27(6):671-5.

Weinmann M, Schuhmacher J, Kummer H, Prinz S, Peng J, Seifert HJ, et al. 2000 Synthesis and thermal behavior of novel si-B-C-N ceramic precursors. Chemistry of Materials. 12(3):623-32.

Zhang H, Pantano CG. 1992 High temperature stability of oxycarbide glasses. Materials Research Society Symposium Proceedings, 271(Better Ceramics through Chemistry V), 783-8.

Ziegler G, Kleebe H-, Motz G, Müller H, Traßl S, Weibelzahl W. 1999 Synthesis, microstructure and properties of SiCN ceramics prepared from tailored polymers. Materials Chemistry and Physics. 61(1):55-63.